



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C08G 63/91, 67/04, B05D 7/00 C09D 5/03	A1	(11) International Publication Number: WO 94/11415 (43) International Publication Date: 26 May 1994 (26.05.94)
(21) International Application Number: PCT/US93/09880 (22) International Filing Date: 14 October 1993 (14.10.93) (30) Priority data: 07/974,569 12 November 1992 (12.11.92) US (71) Applicant: THE DOW CHEMICAL COMPANY [US/ US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US). (72) Inventors: GOULD, Michael, L. ; 114 Coffee Lane, Lake Jackson, TX 77566 (US). GRILLI, David, A. ; 123 Ca- cao, Lake Jackson, TX 77566 (US). DETTLOFF, Mar- vin, L. ; 205 Basswood, Lake Jackson, TX 77566 (US). HICKNER, Richard, A. ; 119 Bougainvillea, Lake Jack- son, TX 77566 (US). RABON, James, A. ; 1309 Rev. Swinney, West Columbia, TX 77486 (US).		(74) Agent: MAURER, Charles, J., III; The Dow Chemical Company, Patent Department, P.O. Box 1967, Midland, MI 48641-1967 (US). (81) Designated States: AU, BR, CA, JP, KR, NO, NZ, Euro- pean patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>With amended claims.</i>
(54) Title: CURABLE COMPOSITION CONTAINING ANHYDRIDE RESINS (57) Abstract Compositions of coreactant resins and polyanhydrides that contain a central moiety and more than one non-cyclic anhy- dride moiety are cured to provide coatings that have good exterior durability. Preferred high molecular weight polyanhydrides contain a central polymer moiety that has no more than 25 weight percent repeating units derived from unsaturated aliphatic hy- drocarbon monomers. In other preferred polyanhydrides, the anhydride moieties are linked to a central moiety by an ester moi- ety.		

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CURABLE COMPOSITION CONTAINING ANHYDRIDE RESINS

The present invention relates to the art of coating compositions.

5 It is known to apply clear and/or colored coatings to metallic and other articles compositions in order to improve durability and appearance, protect, finish and prevent oxidation of metals. For instance, the exterior panels of many automobiles and other outdoor articles are coated with a multilayer finish that contains: (1) a color coat or basecoat layer and (2) a clear coat layer. See, for example, Blackburn et al., U.S. Patent 4,732,791 (March 22, 1988).

10 A common coating composition contains epoxy resins and polymers which contain cyclic anhydrides, such as maleic anhydride and itaconic anhydride polymers and copolymers. See, for example, Corcoran, U.S. Patent 4,816,500 (March 28, 1989); Barsotti et al., U.S. Patent 4,906,677 (March 6, 1990); and Schimmel, U.S. Patent 4,927,868 (May 22, 1990); and Mika & Bauer, "Curing Agents and Modifiers," Epoxy Resins Chemistry and Technology, 485-92 (Marcel Dekker, Inc. 1988). The components are usually applied in an organic solvent and cured
15 using a catalyst. These coatings are frequently used in outdoor applications, such as clear and color coating on automobiles, storage tanks, rail cars, ships, bridges and utility structures.

Public concerns over the emission of volatile organic compounds have made it desirable to coat such articles using a composition that has a very high solids content. At the
20 same time, it is desirable for the resulting coatings to have at least about equivalent performance in terms of appearance and exterior durability. What are needed are new resins that can perform acceptably using low levels of organic solvent.

One aspect of the present invention is a curable composition comprising:

- (a) a polyanhydride resin; and
- 25 (b) at least one resin that reacts with the polyanhydride resin to cure under curing conditions

characterized in that the polyanhydride resin contains: (1) a central moiety, and (2) on average, more than 1 pendant, non-cyclic anhydride moiety bonded to each central moiety.

A second aspect of the present invention is a polyanhydride that comprises:

- 30 (a) a polyvalent organic moiety (A);
- (b) a plurality of ester linkages bonded to the polyvalent organic moiety;
- (c) divalent organic moieties (Q) bonded to the ester linkages; and
- (d) non-cyclic anhydride moieties bonded to the divalent organic moieties.

A third aspect of the present invention is a polyanhydride comprising:

- 35 (a) a central moiety; and
- (b) on average more than 2 pendant, non-cyclic anhydride moieties linked to the central moiety,

characterized in that the central moiety contains a polymer that has a molecular weight of at least 1000 and that contains no more than 25 weight percent of monomer units derived from unsaturated aliphatic hydrocarbon monomers.

5 A fourth aspect of the present invention is a cured composition of the present invention.

A fifth aspect of the present invention is a method or process to coat a substrate, by the steps of:

- (a) applying a curable composition that contains a polyanhydride resin and at least one coreactant resin to a substrate; and
- 10 (b) heating the composition applied in Step (a) to cure, characterized in that the polyanhydride resin contains: (1) a central moiety, and (2) on average, more than 1 pendant, non-cyclic anhydride moiety bonded to each central moiety.

A sixth aspect of the present invention is a coated article containing: (1) a substrate, and (2) a coating on the substrate having at least one layer, characterized in that the
15 coating contains a cured composition of the present invention.

The coating compositions of the present invention can be used in mixtures with relatively high solids content for coating substrates. The mixtures usually have a relatively low viscosity. As added advantages, the mixtures frequently have a long shelf stability, and the coatings frequently have good gloss and distinctness of image. They may also have good
20 chemical etch resistance and exterior durability.

Coreactant Resins

Compositions of the present invention contain one or more resins that react with the polyanhydride to cure under a variety of conditions. Although a broad number of resins are useful for this purpose, the coreactant resin is preferably an epoxy resin, a polyol resin, a
25 polyamine or a mixture containing at least one of those resins. The coreactant resin most preferably comprises an epoxy resin, either alone or in a mixture with the polyamine or polyol resin. Preferred polyol resins include acrylic polyol, hydroxy-containing polyester resins and polyhydroxy polyether resins. Preferred polyamine resins include acrylic polyamine resins and "blocked" amine resins. The most preferred coreactant resin is an epoxy resin.

30 Suitable coreactant coating resins are well known in the art. Examples of suitable polyol resins are described in Shalati et al., U.S. Patent 4,781,806 (October 3, 1989); Shalati et al., U.S. Patent 5,043,220 (August 23, 1991); Claar et al., U.S. Patent 4,798,746 (January 17, 1989); Andrews et al., U.S. Patent 4,826,921 (May 2, 1989); and Marrion et al., U.S. Patent 4,452,948 (June 5, 1984). The number average molecular weight of the polyol resin is
35 preferably at least 200 and preferably no more than 12,000.

Examples of suitable polyamine resins are described in Hutton et al., U.S. Patent 4,043,956 (August 23, 1977); Wellner et al., U.S. Patent 4,279,793 (June 26, 1990); Wellner et al., U.S. Patent 4,970,270 (November 13, 1990); Wellner et al., U.S. Patent 4,975,493 (December 4,

1990); and Blum et al., German Patent 3,819,942 (January 24, 1990). The number average molecular weight of the polyamine resin is preferably at least 200 and preferably no more than 12,000.

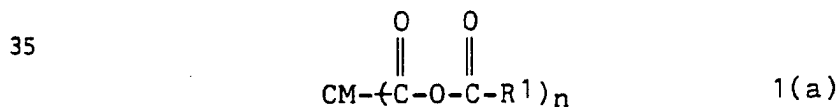
Examples of suitable epoxy resins and typical conditions for their use are described in Corcoran, U.S. Patent 4,816,500 (March 28, 1989); Barsotti et al., U.S. Patent 4,906,677 (March 6, 1990); Schimmel, U.S. Patent 4,927,868 (May 22, 1990); Blackburn et al., U.S. Patent 4,732,791 (March 22, 1988); Blackburn et al., U.S. Patent 4,755,581 (July 5, 1988); Chatta et al., U.S. Patent 4,710,543 (December 1, 1987); Ambrose et al., U.S. Patent 4,749,743 (June 7, 1988) and Tess, "Epoxy Resin Coatings," Epoxy Resins Chemistry and Technology, 719-82 (Marcel Dekker, Inc. 1988).

Examples of suitable epoxy resins include glycidyl ethers created by the reaction of epichlorohydrin and related compounds with phenolic compounds, such as bisphenols, novolacs, resorcinol and hydroquinone, or with aliphatic diols. Other suitable epoxy resins can be the glycidyl ether or ester products of reaction of epichlorohydrin with organic polyacid compounds, such as aliphatic acids (for example glutaric, adipic, azelaic acids); cycloaliphatic acids (for example cyclohexane dicarboxylic acid or cyclohexane tricarboxylic acid); polymerizable acids (such as methacrylic acid); dimerized fatty acids; and aromatic polyacids (for example phthalic, trimellitic and benzene-tetracarboxylic acids). Other suitable epoxy resins are the product of peroxidation of compounds that contain allylic double bonds or internal cyclic double bonds. Other suitable resins contain glycidyl ether or ester moieties and organosiloxane moieties, as described in Liao et al., U.S. Patent 5,206,312 (April 27, 1993) and Liao et al., U.S. Patent 5,188,903 (February 23, 1993). Aliphatic epoxy resins are preferred in many outdoor uses.

The epoxy equivalent weight of the resin (based on 100 percent solids) is preferably at least 100 and more preferably at least 130. It is preferably at most 3000, and more preferably at most 1500. The invention is useful with a broad range of epoxy resins, but the number average molecular weight of the epoxy resin is preferably at least 140 and more preferably at least 200. The molecular weight is preferably no more than 10,000.

Polyanhydrides

The present invention also uses polyanhydride resins that contain more than one pendant, non-cyclic anhydride group linked to a common central moiety. The polyanhydride is an asymmetrical anhydride, and preferably contains a moiety represented by Formula 1(a):



wherein (CM) is a central moiety, (R¹) is a hydrogen atom or an organic moiety, and n is a number of pendant anhydride groups that averages greater than one.

The central moiety may be a simple organic moiety, such as an aliphatic, cycloaliphatic or aromatic moiety, with a plurality of anhydride groups bonded to it.

- 5 Alternatively, it may be a polymer or oligomer that contains a plurality of repeating units which are bonded to one or more pendant anhydride groups. (As used in this application, the term "polymer" shall include oligomers and copolymers unless otherwise stated.) Examples of suitable non-polymer central moieties include multivalent phenyl, t-butyl, neopentyl and cyclohexyl structures. Examples of suitable polymeric central moieties include polymers of
10 styrene, acrylic and methacrylic acid and their esters, and/or other ethylenically-unsaturated monomers.

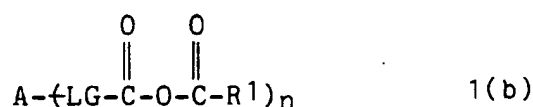
- The central moiety is linked to more than one non-cyclic anhydride moiety, on average. It is preferably linked to at least 2 non-cyclic anhydride groups on average and more preferably to at least 3 non-cyclic anhydride groups on average. The maximum number of non-
15 cyclic anhydride groups is not critical to the invention, and is limited mostly by practical considerations, such as the molecular weight and anhydride equivalent weight of the system. The central moiety is preferably linked to no more than 50 non-cyclic anhydride groups, more preferably no more than 20 and most preferably no more than 10. The anhydride equivalent weight (formula weight per anhydride group) is preferably at least 200 and preferably no more
20 than 1500.

Each anhydride moiety is typically terminated by a hydrogen atom or an organic group (R¹). It is preferably terminated by an organic group. This group is preferably aliphatic and more preferably alkyl. It preferably contains no more than 6 carbon atoms, more preferably no more than 4 carbon atoms and most preferably no more than 1 carbon atom.

- 25 The terminating group may also contain a ketone or aldehyde functionality, as in the reaction product of a carboxylic acid and a diketene, which results in an acetoacetic anhydride group.

The anhydride moiety need not be bonded directly to a polymer or oligomer backbone. The polyanhydride may optionally contain a polyvalent organic moiety (A) that is linked to a plurality of anhydride groups by a plurality of pendant linking groups (LG), as

- 30 illustrated in Formula 1(b):

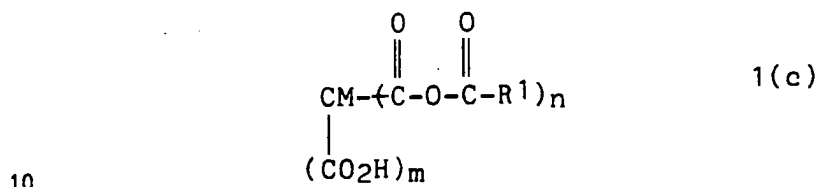


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The linking group (LG) may contain, for example, ester linkages, alkylene groups, ether linkages, urethane linkages and combinations of those. The polyvalent organic group may contain, for example, a polymer or a polyvalent alkyl or aromatic group. The combination

of the polyvalent organic moiety (A) and the linking groups (LG) forms the central moiety (CM) as previously described.

The central moiety may optionally contain other functional groups in addition to the pendant non-cyclic anhydride groups. For example, the central moiety may contain
 5 pendant acid groups, so that the anhydride is represented by Formula 1(c):



wherein m is a number of pendant acid groups and all other characters have the meaning previously given. The molar ratio of pendant non-cyclic anhydride groups to pendant acid
 15 groups in the polyanhydride is preferably at least 25:75, more preferably at least 50:50, and more highly preferably at least 75:25. Most preferably, the polyanhydride contains essentially no pendant acid groups (0:100 ratio).

The central moiety may also contain cyclic anhydride moieties. Preferably, at least 50 percent of the anhydride moieties are non-cyclic, more preferably at least 75 percent are
 20 non-cyclic, more highly preferably at least 95 percent are non-cyclic and most preferably essentially all (100 percent) are non-cyclic. If the central moiety is a polymer, then the backbone repeating units are preferably not linked by anhydride linkages, like polyanhydrides described in Pettit et al., U.S. Patent 5,055,524 (October 8, 1991). Anhydride linkages between repeating units may also react during curing of the resin.

The preferred molecular weight of the polyanhydride varies depending upon the
 25 molecular weight of the coreactant resin. Preferably, if the coreactant resin is a higher molecular weight resin (number average molecular weight of 2000 to 10000), then the polyanhydride resin is preferably a low molecular weight resin (average molecular weight of 1500 or less). If the coreactant resin is a lower molecular weight resin (average molecular weight of no more than 2000), then the polyanhydride resin is preferably a higher molecular
 30 weight resin (average molecular weight of 2000 or greater). Usually, the average molecular weight of the polyanhydride resin is preferably between 400 and 10,000.

Many different polyanhydrides that fall within the broad description can provide the desired high solids formulations and high exterior durability of the present invention.
 35 However, certain selections of central moiety (CM) and number of pendant anhydride groups (n) are preferred. The preferred description of the polyanhydride changes depending upon its molecular weight.

(A) Higher Molecular Weight Anhydrides

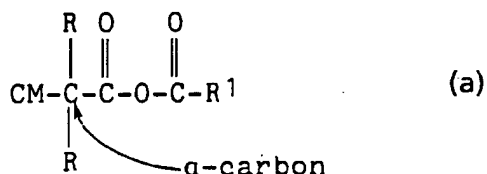
When the central moiety is a polymer or oligomer, the number of monomer units derived from ethylene, propylene and other aliphatic hydrocarbon α -olefins is preferably minimized. Polymers with a high content of ethylene or propylene monomer units do not usually form high solids solutions in common solvents. The polymer preferably contains no more than 50 weight percent aliphatic hydrocarbon monomer units, more preferably no more than 25 weight percent, more highly preferably no more than 10 weight percent, and most preferably essentially none. Monomer units derived from acrylic acid, methacrylic acid and their esters provide greater solubility. They preferably make up at least 50 weight percent of the polymer and more preferably at least 75 weight percent. Polyester polymers also usually have good solubility, and so they make good central moieties.

Styrenic monomer units frequently improve the solubility of the polymer, but they may also worsen the exterior durability of the cured coating. The central moiety preferably contains no more than 25 weight percent aromatic units, such as are derived from styrene, more preferably no more than 20 weight percent, and most preferably no more than 15 weight percent aromatic units.

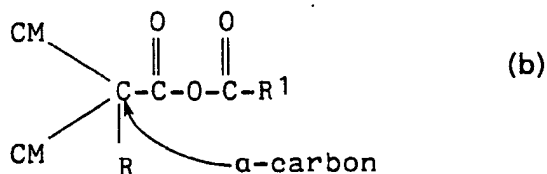
It is theorized that the exterior durability of the cured coating may also be improved if the α -carbon atoms which link the anhydride groups to the central moiety are quaternary carbon atoms, that is, not bonded to a hydrogen atom. Preferably at least 50 percent of the α -carbon atoms are quaternary, more preferably at least 75 percent are quaternary, more highly preferably at least 90 percent are quaternary and most preferably essentially all are quaternary. Examples of suitable quaternary α -carbon atoms are set out in Formulae 2(a) and (b):

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wherein (CM) represents the central moiety and each (R) represents an aliphatic group, which is preferably alkyl and more preferably lower alkyl (1 to 6 carbon atoms). For instance, the pendant linear anhydride groups may be bonded to units derived from methacrylic acid, rather than to units derived from acrylic acid.

5 The number average molecular weight of the central moiety is preferably at least 1000 and more preferably at least 1500. Examples of processes used to make high molecular weight anhydrides are described in numerous references, such as Maloney, U.S. Patent 3,523,930 (August 11, 1970); Vaughn et al., U.S. Patent 3,631,156 (December 28, 1971); Vaughn, U.S. Patent 3,631,157 (December 28, 1971); Vaughn, U.S. Patent 3,803,087 (April 9, 10 1974); and Vaughn, U.S. Patent 4,308,363 (December 29, 1981). These references teach that polyanhydrides can be made by reacting: (a) a polyacid that has more than two pendant acid groups; with (b) an acylating agent such as an anhydride, an acid halide or a ketene.

The polyacid is preferably highly soluble in at least some common solvents, such as hydrocarbon solvents (for example toluene or xylene), chlorinated hydrocarbons, ketones, 15 esters, glycol ethers, polyethers (for instance, glyme or diglyme) or common polar aprotic solvents. It preferably forms mixtures in at least one of those solvents at about room temperature that contain at least 50 weight percent solids, more preferably at least 60 weight percent and most preferably at least 70 weight percent. Solubility can be measured using any of those solvents, but it is conveniently measured in xylene.

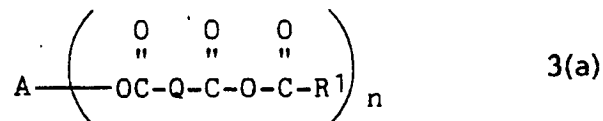
20 Suitable polyacids can be made by several different methods, such as by polymerization of polymers and copolymers containing acrylic or methacrylic acid. Many polymers of acrylic and methacrylic acid are commercially available, and others can be synthesized by well known processes. See, for example, 1 Encyclopedia Poly. Sci. & Eng. (2d Ed.), Acrylic and Methacrylic Acid Polymers, at 221-224 (J. Wiley & Sons 1985).

25 (B) Lower Molecular Weight Anhydrides

Lower molecular weight anhydrides preferably contain:

- (a) a polyvalent organic moiety (A);
- (b) a plurality of ester linkages bonded to the polyvalent organic moiety;
- (c) divalent organic moieties (Q) bonded to the ester linkages; and
- 30 (d) non-cyclic anhydride moieties bonded to the divalent organic moieties.

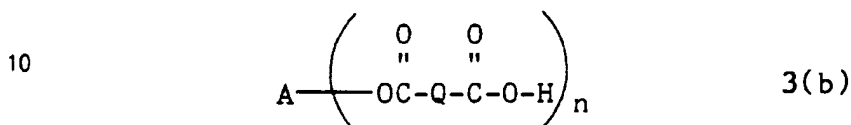
For example, the lower molecular weight anhydride is preferably represented by Formula 3(a):



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wherein (A) is the polyvalent organic moiety, (Q) is the divalent organic moiety, and all other characters have the meaning previously described. Of course, the polyvalent organic moiety (A), the ester linkages and the divalent moieties (Q) in combination form the central moiety (CM) previously described. (A) may also contain, or be linked to, other pendant, non-linear anhydride moieties which are not linked by an ester moiety.

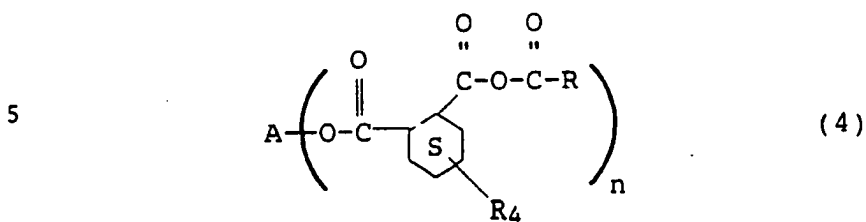
The preferred lower molecular weight anhydrides can be made from a corresponding polyacid (see Formula 3(b)), using the same anhydride-forming reactions that were previously described:



The polyacid can be made by reacting a cyclic anhydride with a polyol. See, for example, Singer et al., U.S. Patent 4,703,101 (October 27, 1987) and Schimmel et al., U.S. Patent 4,927,868 (May 22, 1990). In the resulting acid, the polyvalent organic moiety (A) is derived from the polyol, and the divalent organic moiety (Q) is derived from the cyclic anhydride. Examples of suitable polyols include phloroglucinol, diresorcinol, glycols, glycerine, trimethylolpropane, pentaerythritol, sorbitol, glucose and/or other sugars. Examples of suitable cyclic anhydrides include maleic, succinic, itaconic, citraconic, glutaric, phthalic and hexahydrophthalic anhydride.

Each (A) and (Q) is preferably aliphatic, aromatic or aliphatic-aromatic. Each aliphatic group is preferably alkyl. Each (A) and (Q) preferably contains no more than about 12 carbon atoms and more preferably no more than 7 carbon atoms. On average the central moiety is preferably linked to at least 3 pendant anhydride groups, and more preferably at least 4 pendant anhydride groups. On average, it is preferably linked to at most 6 anhydride groups and more preferably at most 4 anhydride groups. A highly preferred lower-molecular weight polyanhydride is represented by Formula 3(a) wherein (A) is an aliphatic moiety and (Q) is a cycloaliphatic moiety. The most preferred cycloaliphatic group is a divalent cyclohexane group. The ester and anhydride are preferably in a 1,2-position with respect to each other. The terminating aliphatic group bonded to the anhydride is preferably a lower (C₁-C₆) alkyl group and is most preferably a methyl group.

The low molecular weight polyanhydride is preferably represented by Formula 4:



or a substituted variation thereof, wherein (A) is an alkyl group, each R is a hydrogen atom or a lower (C₁-C₆) alkyl group, and n is a number of substituent groups averaging greater than 1. n is preferably on average 3 to 4, inclusive. (A) is preferably a multivalent alkyl group containing 5 to 12 carbon atoms, such as a neopentane group and related alkyl structures. The four R substituents bonded to the cyclohexane ring are preferably hydrogen atoms. It can be synthesized by: (1) reacting a 5 to 12 carbon alkyl polyol (such as pentaerythritol) with hexahydrophthalic anhydride; and (2) reacting the product of that reaction with an acid anhydride (such as acetic anhydride), an acid halide (such as acetyl chloride) or a ketene.

Coating Compositions

Coating compositions of the present invention contain a polyanhydride and a coreactant resin. They may be applied as powder coatings, but they are preferably formulated into high solids coating systems dissolved or suspended in a solvent or a blend of solvents. The solvent is usually organic. Examples of preferred solvents contain aromatic hydrocarbons, such as petroleum naphtha or xylenes; ketones, such as methyl amyl ketone, methyl isobutyl ketone, methyl ethyl ketone or acetone; ester solvents, such as butyl acetate or hexyl acetate; or glycol ether esters, such as propylene glycol monomethyl ether acetate.

The equivalent ratio of the coreactant resin and the polyanhydride resin is preferably at least 0.8:1, more preferably at least 0.9:1 and most preferably at least 1:1. The equivalent ratio is preferably at most 1.3:1, more preferably at most 1.2:1 and most preferably at most 1.1:1. The polyanhydride and coreactant resin may be partially cured before they are applied to a substrate, but they preferably are not.

The composition may contain other suitable additions, such as catalysts, pigments, stabilizers, toughening agents and fillers.

It usually contains a catalyst when it is cured. Examples of suitable catalysts are described in: Smith, U.S. Patent 3,784,583 (January 8, 1974); Smith, U.S. Patent 3,979,355 (September 7, 1976); Marrion et al., U.S. Patent 4,452,948 (June 5, 1984); Shalati et al., U.S. Patent 4,871,806 (October 3, 1989); Lee & Neville, Handbook of Epoxy Resins 12-13 (McGraw-Hill 1967); and Mika & Bauer, Epoxy Resins 487 (Marcel Dekker, Inc. 1988). For example, the catalyst may be a quaternary phosphonium salt (such as triethylphenylphosphonium chloride),

a quaternary ammonium salt (such as tetrabutylammonium bromide), or a tertiary amine (such as dimethylethanolamine). The composition usually contains between 0.1 and 5 weight percent catalyst, based upon the weight of solids.

5 The other materials depend upon its intended use. If the composition is intended for a clear coating, then it preferably does not contain fillers, pigments or other materials that can adversely effect the clarity of the cured coating. On the other hand, if it is intended as a color coating, then it should contain the desired pigments.

The total solids content for a formulation of solvent, coreactant resin, anhydride and other solids in the composition is preferably low enough so that the viscosity of the
10 composition is within a range that is suitable for its intended use. For instance, the viscosity for an air-spraying composition at 25°C is preferably at most 150 cps, more preferably at most 110 cps, and most preferably at most 70 cps; whereas the viscosity of an airless spraying composition at 25°C is preferably at most 5000 cps. The solids content is preferably at least 50 weight percent, more preferably at least 65 weight percent, and most preferably at least 70
15 weight percent. The solids content is preferably as high as practical, but it is usually no more than 95 weight percent (unless the composition is applied as a powder, in which case it contains 100 percent solids).

The composition is applied to a substrate in ordinary ways for coating, such as by conventional spraying, electrostatic spraying, roller coating, dipping or brushing. It is
20 particularly useful as a clear or color coating for outdoor articles, such as automobile and other vehicle body parts. The substrate may be prepared with a primer and/or a color coat or other surface preparation before coating.

The composition becomes a useful thermoset coating by heating at a temperature at which the formulation cures. (The solvent is preferably removed at an elevated
25 temperature either during or before the curing step.) For most resins, that temperature is between 80°C and 180°C, although some coreactant resins can be formulated to cure even at ambient temperature, such as 20°C.

The resulting coated article contains a substrate layer and at least one coating layer that contains a cured composition of the present invention. The layer containing the
30 cured composition need not be adhered directly to the substrate; there may optionally be intervening layers. One preferred coated article system contains:

- (a) the substrate;
 - (b) optionally, a primer or surface treatment layer adhered to the substrate;
 - (c) a color layer adhered either to the substrate or to the primer or surface treatment
35 layer; and
 - (d) a clear coat layer adhered to the primer layer,
- wherein either the color layer or the clear coat layer contains a cured composition of the present invention. The substrate is preferably metallic. The layers that do not contain

compositions of the present invention preferably contain known paints or cured coating resins such as curable epoxy compositions. The color layer preferably contains pigments, and the clear layer preferably does not. The thickness of each layer is dictated primarily by user specifications, and varies depending upon the intended use. Although the thickness is not critical to the invention, for most applications the cured clear or color layer of the present invention is preferably between 0.1 mil (2.5 μm) and 20 mil (500 μm) thick, and more preferably between 1 mil (25 μm) and 5 mil (130 μm) thick.

The cured composition preferably has a gloss of at least 80 percent, and more preferably at least 90 percent, as measured by a BYK MULTIGLOSS multiangle gloss meter at 20° normal to the surface. Its distinctness of image is preferably at least 85 and more preferably at least 90, as measured by a DORI-GON D47-6 meter manufactured by Hunter Laboratories. Its exterior durability may be tested by common "accelerated" test methods such as with a Cleveland Q-Panel QUV unit. The results of such tests (for a UV-stabilized coating) are preferably less than 20 percent loss of gloss (measured at 20° normal to the panel surface) after 3000 hours of irradiation at either 313 nm or 340 nm.

The compositions of the present invention can easily be formulated with high solids content, so that lower quantities of solvent can be used if desired. They can be cured to provide coatings with superior exterior durability.

The invention is further illustrated by the following examples.

20 Illustrative Examples

The following examples are for illustrative purposes only. They should not be taken as limiting the scope of either the specification or the claims. Unless stated otherwise, all parts and percentages are by weight.

Example 1 - Coating Composition Containing Epoxy Resin and Anhydride Oligomer

25 Equimolar portions of pentaerythritol and trimethylolpropane were placed in a reactor. A blend of 70 percent methylhexahydrophthalic anhydride and 30 percent hexahydrophthalic anhydride was added in stoichiometric quantities to the reactor. The mixture is heated and stirred at 170°C until it becomes clear. A mixture of xylenes was added to make an 80 percent solids mixture. A catalytic amount of dimethylaminopyridine was added and the reaction was continued at 135°C for three hours. The acid equivalent weight is determined by titration with aqueous potassium hydroxide.

30 A portion of the mixture containing 10.25 equivalents of acid was diluted with xylenes to 60 percent solids. A 1.3x stoichiometric quantity of acetic anhydride was added and the mixture was stirred for fourteen hours. The pressure was reduced to 300 mmHg and the temperature was increased to 60°C for 2 hours. A 500 g quantity of xylenes was added to maintain an azeotropic distillation of 3 mL/min. over a period of four hours. After the distillation, the reactor was fitted with a Soxhlet extractor that contained 3 mol of anhydrous sodium carbonate. The temperature was increased to 75°C and the pressure was reduced

slowly to 90 mmHg. The "closed" system was then allowed to reflux for several hours, during which time acetic acid reacted with sodium carbonate in the extractor thimble to an acceptable minimum. The resulting pale yellow resin had a Gardner color of 1 and a Brookfield viscosity of 885 cps at 25°C. Its theoretical anhydride equivalent weight was 349 at 65.5 percent solids.

5 550 parts of the anhydride resin were formulated with 206 parts diglycidyl cyclohexane dicarboxylate, 6.7 parts quaternary ammonium catalyst, 22.2 parts hydroxybenzotriazole UVA, 14.8 parts HALS, 1.5 parts flow modifier and 150 parts propylene glycol methyl ether acetate. The mixture was applied by spray at 63.8 percent solids concentration to steel panels precoated with a waterborne white enamel basecoat. After two
10 minutes flash time, the panels were heated to 135°C for 30 minutes to cure.

The properties of the cured coating are tested and are set out in Table 1.

TABLE 1

	<u>Test</u>	<u>Result</u>
15	MEK double rubs	100 + (no marring)
	Knoop Hardness	6.6 \pm 0.5
	Average film thickness	50.5 μ m (1.99 mil)
	Hunter Δ B (yellowness)	1.2 \pm 8.5%
20	24 hour 5% NaOH	no stain, mar or erosion
	24 hour 5% HCl	no stain, mar or erosion
	20° Gloss	83 \pm 1
	Distinctness of Image	87 \pm 1

25 Example 2 - Coating Composition Containing Epoxy Resin and Anhydride Polymer

A copolymer containing 40 weight percent methacrylic acid and 60 weight percent butyl acrylate was prepared according to the process described in U.S. Patent 4,906,677. A 51 percent solution of the resin in a mixture of xylenes, butyl acetate and propylene glycol monomethylether acetate was heated to 125°C, and the reactor was sparged
30 with nitrogen to remove volatiles. 1.1 equivalents of acetic anhydride was added dropwise over 1.66 hours, and heating was continued for another 5 hours. During this time, 100 mL of propylene glycol methyl ether acetate was added to maintain temperature at 125°C and 280 mL of acetic acid/solvent azeotrope was recovered. The resulting solution contained 59.4 percent polyanhydride with an anhydride equivalent weight of 974 and an acid equivalent weight of
35 627, as determined by titration.

A composition that contains 88.7 parts polyanhydride, 37.0 parts diglycidyl cyclohexane dicarboxylate, 1.05 parts triethylenediamine and 6.9 parts mixed xylenes was formulated. The composition was applied, cured at 121°C and tested as described in Example 1. The results are set out in Table 2:

TABLE 2

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	<u>Test</u>	<u>Result</u>
	MEK double rubs	200 + (no marring)
	Knoop Hardness	5.2
10	Average film thickness	65.0 μ m (2.56 mil)
	Hunter Δ B (yellowness)	1.35 \pm 0.13%
	24 hour 5% NaOH	no stain, mar or erosion
	24 hour 5% HCl	no stain, mar or erosion

15 Example 3 - Coating Composition Containing Epoxy Resin, Polyol Resin and Anhydride Oligomer

An anhydride resin was made from pentaerythritol, methylhexahydrophthalic anhydride, hexahydrophthalic anhydride and ketene. The anhydride was represented by Formula 4, wherein (A) was a neopentyl group and (n) was 4. The resin had an anhydride
20 equivalent weight of 348, and showed almost no acid - as measured by titration and infrared analysis.

40 parts anhydride resin were formulated with 18.4 parts diglycidyl cyclohexane dicarboxylate, 31.6 parts DESOMOPHEN 651A-65PMA hydroxy-functional polyester resin, 0.2 parts phosphonium halide catalyst, 0.4 parts flow modifier and 30 parts solvent mixture of
25 xylenes, propylene glycol methyl ether acetate and butyl acetate. The formulation has a Zahn #2 viscosity of 25 seconds.

The formulation was applied by spray to steel panels precoated with a waterborne white enamel basecoat. After five minutes flash time, the panels were heated to 135°C for 60 minutes to cure. The results are set out in Table 3:

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TABLE 3

	<u>Test</u>	<u>Result</u>
	MEK double rubs	200 + (slight marring)
5	Knoop Hardness	12.3
	Average film thickness	70.6 μm (2.78 mil)
	Hunter ΔB (yellowness)	0.74 \pm 0.04%
	24 hour 5% NaOH	no stain, mar or erosion
	24 hour 5% H ₂ SO ₄	no stain, mar or erosion
10	20° Gloss	84
	Distinctness of Image	77

Example 4 - Coating Composition Containing Epoxy Resin, Polyamine Resin and Anhydride Oligomer

15 An anhydride resin was made as described in Example 3.

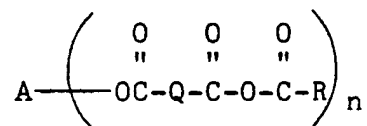
50 parts anhydride resin were formulated with 23 parts diglycidyl cyclohexane dicarboxylate, 16.5 parts ANCAMIDE 2353X polyamine resin, 0.39 parts phosphonium halide catalyst and 55 parts propylene glycol methyl ether acetate. The formulation has a Zahn #2 viscosity of 23 seconds.

20 The formulation was applied by spray to steel panels precoated with a waterborne white enamel basecoat. After five minutes flash time, the panels were heated to 135°C for 30 minutes to cure. The results are set out in Table 4:

TABLE 4

	<u>Test</u>	<u>Result</u>
	MEK double rubs	200 + (slight marring)
	Knoop Hardness	14.1
	Average film thickness	77.5 μm (3.05 mil)
30	Hunter ΔB (yellowness)	5.79 \pm 0.18%
	24 hour 5% NaOH	no stain, mar or erosion
	24 hour 5% H ₂ SO ₄	no stain, mar or erosion
	20° Gloss	83
35	Distinctness of Image	83

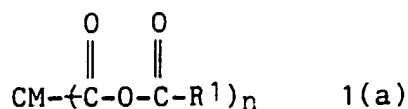
1. A curable composition comprising:
 - (a) a polyanhydride resin; and
 - (b) at least one coreactant resin that reacts with the polyanhydride resin under curing conditions,
- 5 characterized in that the polyanhydride resin contains: (1) a central moiety, and (2) on average, more than 1 pendant, non-cyclic anhydride moiety bonded to each central moiety.
2. A method to coat an article, comprising the steps of:
 - (a) applying a curable composition, which contains a polyanhydride and at least one coreactant resin to a substrate; and
 - 10 (b) heating the composition applied in Step (a) to cure the composition
- characterized in that the polyanhydride resin contains: (1) a central moiety, and (2) on average, more than 1 pendant, non-cyclic anhydride moiety bonded to each central moiety.
3. A curable composition or method as described in any of the previous Claims, wherein the curable composition is in the form of a powder.
- 15 4. A curable composition or method as described in any of the previous Claims wherein the curable composition further comprises a solvent, and the composition has a solids content of at least 55 weight percent.
5. A curable composition or method as described in any of the previous Claims wherein the coreactant resin contains an epoxy resin.
- 20 6. A curable composition or method as described in Claim 5 wherein the coreactant resin further contains a polyol resin or a polyamine resin.
7. A curable composition or method as described in any of the previous Claims wherein the polyanhydride resin contains on average more than 2 anhydride moieties per molecule.
- 25 8. A curable composition or method as described in any of the previous Claims wherein the polyanhydride resin comprises a moiety represented by the Formula:



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wherein:

- (A) is a multivalent organic moiety;
 - (Q) is a divalent organic moiety;
 - (R) is a hydrogen atom or an organic moiety; and
 - 35 n is a number of pendant groups that is at least 2.
9. A curable composition or method as described in any of the previous Claims wherein the polyanhydride resin contains a moiety represented by the Formula:



5. wherein (CM) contains a polymer which has a number average molecular weight of at least 1000, (R¹) is a hydrogen atom or an organic moiety, and n is a number or anhydride moieties.

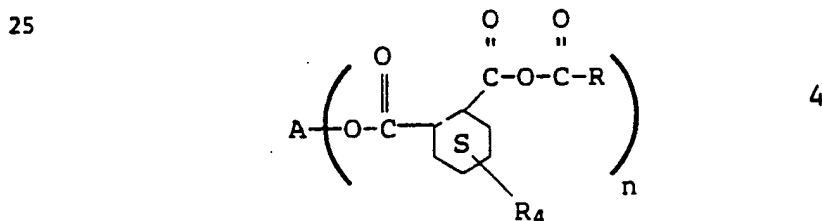
10. A coated article that contains:

- (a) a substrate;
 10 (b) optionally, a primer or surface treatment layer adhered to the substrate;
 (c) a color layer adhered either to the substrate or to the primer or surface treatment layer; and
 (d) a clear coat layer adhered to the primer layer,
 characterized in that either the color layer or the clear coat layer or both contain the cured
 15 product of a composition as described in any of Claims 1 or 3-9.

11. A polyanhydride comprising:

- (a) a polyvalent organic moiety;
 (b) a plurality of ester linkages bonded to the polyvalent organic moiety;
 (c) divalent organic moieties bonded to the ester linkages; and
 20 (d) non-cyclic anhydride moieties bonded to the divalent organic moieties.

12. A polyanhydride as described in Claim 11 or a curable composition or method as described in any of Claims 1-8 or a coated article as described in Claim 10, wherein the polyanhydride is represented by the formula:



wherein (A) is an alkyl group, each R is a hydrogen atom or a lower alkyl group, and n is a number of substituent groups averaging greater than 1.

13. A polyanhydride comprising:

- 35 (a) a central moiety; and
 (b) on average more than 2 pendant, non-cyclic anhydride moieties linked to the central moiety,

characterized in that the central moiety contains a polymer that has a molecular weight of at least 1000 and that contains no more than 25 weight percent of monomer units derived from unsaturated aliphatic hydrocarbon monomers.

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AMENDED CLAIMS

[received by the International Bureau on 29 March 1994 (29.03.94);
original claim 5 deleted; original claims 1,2 and 6 amended;
remaining claims unchanged (1 page)]

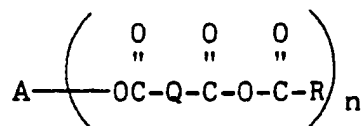
1. A curable composition comprising:
 - (a) a polyanhydride resin; and
 - (b) an epoxy resin,

5 characterized in that the polyanhydride resin contains: (1) a central moiety, and (2) on average, more than 1 pendant, non-cyclic anhydride moiety bonded to each central moiety.
2. A method to coat an article, comprising the steps of:
 - (a) applying a curable composition, which contains a polyanhydride and at least one epoxy resin to a substrate; and
 - 10 (b) heating the composition applied in Step (a) to cure the composition

characterized in that the polyanhydride resin contains: (1) a central moiety, and (2) on average, more than 1 pendant, non-cyclic anhydride moiety bonded to each central moiety.
3. A curable composition or method as described in any of the previous Claims, wherein the curable composition is in the form of a powder.
- 15 4. A curable composition or method as described in any of the previous Claims wherein the curable composition further comprises a solvent, and the composition has a solids content of at least 55 weight percent.
5. Cancelled
6. A curable composition or method as described in any of the previous claims

20 wherein the composition further contains a polyol resin or a polyamine resin.
7. A curable composition or method as described in any of the previous Claims wherein the polyanhydride resin contains on average more than 2 anhydride moieties per molecule.
8. A curable composition or method as described in any of the previous Claims

25 wherein the polyanhydride resin comprises a moiety represented by the Formula:



30 wherein:

- (A) is a multivalent organic moiety;
 - (Q) is a divalent organic moiety;
 - (R) is a hydrogen atom or an organic moiety; and
 - n is a number of pendant groups that is at least 2.
- 35 9. A curable composition or method as described in any of the previous Claims wherein the polyanhydride resin contains a moiety represented by the Formula:

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 93/09880

A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 C08G63/91 C08G67/04 B05D7/00 C09D5/03

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C08G C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,3 360 543 (HOY) see example 4 -----	1-11
X	US,A,1 993 828 (BRUBAKER ET AL) see page 2, right column, line 30; claim 9 -----	1-10

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

21 January 1994

Date of mailing of the international search report

18.02.94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Schueler, D

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 93/09880

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-3360543		NONE	
US-A-1993828		NONE	